

New Way of Production of Cyclopentanone

Ján Vojtko

*Slovak Technical University, Faculty of Chemical and Food Technology,
Department of Organic Technology,
Radlinského 9, 81237 Bratislava, Slovak Republic
e-mail: jan.vojtko@stuba.sk*

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Abstract

The paper describes the mode of preparation of cyclopentanone. The principle of this procedure lies in pyrolysis /thermic decarboxylation/ and simultaneously run hydrolysis of the reaction mixture. The reaction mixture consists of dimethyl adipate, methyl hydrogen adipate and adipic acid, together with methanol and water. The reactions runs on heterogeneous catalyst at temperatures around 450°C

Key words: Cyclopentanone, pyrolysis of adipic acids and its esters

Introduction

Cyclopentanone is a colourless liquid of typical odour, with boiling point of 130.65 °C at normal pressure. Contrary to the well-known cyclohexanone, that is an important resource for production of polyamides, cyclopentanone for its limited availability is produced as a chemical speciality. Among the most important ways of its usability is the production of jasmine ketone "Jasmon". In such production cyclopentane is an intermediate product widely used in cosmetics ^[1]. Its chemical structure is *cis*-3-methyl-2-(2-pentenyl)-2-cyclopentenyl-1-on, with the typical odour after jasmine.

In the cosmetic industry also other derivatives are used out of which cyclopentanone is an intermediate product. From the whole array of products these are namely: "Dihydrojasmon" /3-methyl-2-pentyl-cyclopentene-1-on/, "Isojasmon" /2-hexyl-2-cyclopentene-1-on/, "Delphone" /2-pentylcyclopentanone/, "Velou-tone" /trimethylpentylcyclopentanone/, etc.

Besides the most common applications in cosmetic products and products for personal hygiene (soaps), cyclopentanone is used in some pesticides, pharmaceuticals and as a special solvent in the electronics industry.

Cyclopentanone can be prepared from different resources by several methods.

One of the methods represents analogical preparation of cyclohexanone from cyclohexanol. The resource is cyclohexanol that is dehydrogenated at 260°C on Cu-Zn catalyst at volumetric load 5 hour⁻¹ with 22% yield of cyclopentanone ^[2].

Oxidation of cyclopentanol in methylenchloride on catalysis of barium-manganate leads to the origin of cyclopentanone in 72% yield ^[3].

To prepare cyclopentanone the oxidation of cyclopentane could also be suitable under the conditions similar to oxidation of cyclohexane. However, the process would need higher pressures because of high volatility of cyclopentane. Because the oxidation of cyclohexane has low selectivity, the method could be applicable only for bulk processes.

Other procedures for producing cyclopentanone are based on isomerization of cyclopentenoxide. Thus, on isomerization of cyclopentenoxide in n-hexane in hydrogen atmosphere at 70°C and under catalysing 5% of Pd on aluminium oxide at 92.2% conversion, there occur 58.3% molar cyclopentanone and 32.1% cyclopentanol ^[4].

Cyclopentene can equally be used for the synthesis of cyclopentanone. In the process, analogical to Wacker's procedure for production of acetaldehyde, on applying PdCl₂ and FeCl₃ in liquid phase, in this case occurs cyclopentanone in 90% selectivity at 50% conversion of cyclopentene^[5].

To prepare cyclopentanone, some long-known procedures for preparing ketones on pyrolysis of calcium or barium salts of carboxylic acids can be used. Cyclopentanone can be produced from adipic acid with under-stoichiometric amounts of Ba/OH₂^[6].

In the publications of Russian authors^[7] production of cyclopentanone is described as a result of the reaction of adipic acid at temperatures 250 °C – 290 °C with 1 % of Fe₂O₃. The cyclopentanone can be isolated from the reaction mixture by distilling with water vapour.

When adipic acid is heated in high-boiling solvent (liquid paraffin) in the presence of

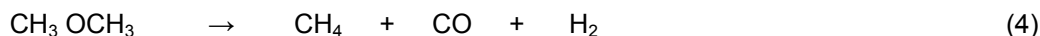
ZrO₂, cyclopentanone occurs alongside with other compounds^[8].

Cyclopentanone can be prepared from adipic acid also by utilising esters of this acid. The patent^[9] issued in Germany describes the preparation of cyclic ketones /CH₂/n-CO, where n = 4 - 6, from esters of the appropriate di-carboxylic acids. The patent^[10] describes preparation of cyclopentanone from dimethyl adipate on zeolite or phosphate catalysts at temperatures 150°C – 450°C in liquid or gaseous phase at selectivity 88% and conversion 87%.

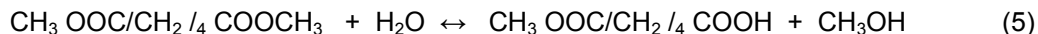
The principle of our way of producing cyclopentanone^[11,12] is the thermal decomposition of mixture. The mixture contains dimethyl adipate, methyl hydrogen adipate and adipic acid, together with methanol and water in gaseous phase at temperatures 250°C – 600°C. The on-going reaction is as follows:



On the reaction the originating dimethyl ether decomposes to:



Simultaneously, by the action of water vapour the esters of adipic acid hydrolyse to:



A great advantage of this way of production (besides high selectivity of production of cyclopentanone) is the fact that by esterification with methanol the crystalline adipic acid is turned to the liquid phase. This mixture is technologically more convenient to manipulate with.

The authors of this paper have paid great attention to the choice of catalyst suitable for the process of pyrolysis (thermic decarboxylation) of esters of adipic acid.

EXPERIMENTAL

Pure adipic acid, methanol r.p., Th/NO₃/₄.12H₂O, Mn/NO₃/₂.6H₂O, Zn/NO₃/₂.6H₂O, Ba/NO₃/₂, Fe/NO₃/₃.9H₂O - all in r.p., clinoptilolite /natural zeolite/ - from Chemko Strážske, purified pumice, waste from production of Al from Žiar nad Hronom.

To analyse the products of pyrolysis gas chromatography was used on the measuring device fy. Carlo Erba Fractovap 2300. The length of the glass column was 1.5m, the inner diameter was 3mm. The column was filled with Chromaton NaW DMCS with 5% OV 17, at temperatures between 80°C and - 170°C.

To check the esterification mixture as a raw material for pyrolysis the common alkalimetric titration for phenolphthalein was used.

Equipment and method

The laboratory pyrolysis reactor consisted of a glass tube with a total length 50cm with inner diameter of 3cm. From the bottom of the body of the reactor a glass tube having the outer diameter of 12 cm was projecting to the height of 30cm from the bottom of the reactor, so that 3/5 of the length of the reactor was annular space. The tube served to take down resistance temperature measurements. The

bottom part of the reactor contained a tube to take away liquid and gaseous damp of pyrolysis.

The reactor was filled with glass beads. Its middle part contained 50g of catalyst over which there were again beads. To the top part of the reactor, which was closed with a ground glass joint, the liquid esterification mixture was led as a raw material with the help of a linear micro-pump. The mixture contained an equilibrium mixture dimethyladipate, monomethyladipate, adipic acid, methanol and water. This mixture was obtained directly from the esterification process after the catalyst katex, used in

esterification, had been filtered off. The whole reactor was inserted into a laboratory pyrolysis furnace that was cylinder-shaped and it was kept at the desired temperature (see Table 1.) $\pm 2^\circ\text{C}$ with the help of a regulator. On the collection tube there was installed an efficient water cooler so that non-condensed gases could be taken to the fume chamber.

The catalyst was prepared in the way that the weighed amount of the carrier (e.g. clinoptilolite) was washed with a solution of the particular salt and after evaporating water it was annealed at 600°C for 1 hour.

RESULTS

The effect of the catalysts can be found in Table 1.

Table 1. Effect of Catalysts on Production of Cyclopentanone.

Catalyst Carrier	Temperature ($^\circ\text{C}$)	Flow ($\text{cm}^3 \cdot \text{min}^{-1}$)	Conversion	Selectivity
ThO ₂ /pumice	395	0,75	65,0	92,8
	440	0,25	87,0	87,5
		0,75	67,9	92,5
MnO ₂ /pumice	350	0,25	9,7	99,0
		0,75	8,3	99,0
	400	0,25	24,5	97,9
		0,75	19,3	97,3
	450	0,25	42,1	85,2
		0,75	23,8	93,2
Fe ₂ O ₃ /zeolite	400	0,25	58,4	94,8
		1,00	27,1	95,7
	425	0,625	32,4	93,7
	454	0,625	39,7	89,7
ZnO/zeolite	400	0,50	23,1	90,5
		1,00	12,6	96,8
	450	0,50	53,7	81,6
Ba/NO ₃ / ₂ /zeolite	420	0,25	16,3	91,7
MnO ₂ /zeolite	350	0,375	29,6	80,7
	400	0,375	58,3	75,0
		0,75	27,7	85,5
	450	0,75	78,7	76,1
Industrial waste	400	0,75	55,5	96,5
	450	0,75	71,2	93,8

Note: The amount of oxide on the carrier in Table 1. after calculating to pure metal was always 10% weight.

The service life of catalyst was monitored on a catalyst of industrial type. In fact it was a mixture of oxides SiO₂, Al₂O₃, Fe₂O₃, TiO₂, that was monitored for 45 hours.

Table 2. Dependence of Production of Cyclopentanone on Time

Temperature	Reaction time, (hours)	Conversion	Selectivity
400	1	56,3	96,6
	10	47,1	96,8
	15	44,3	95,9
	20	44,5	96,1
	30	43,5	95,2
	40	42,8	95,5
	45	39,8	94,0

Note: The flow of the raw material during measurements was $0.75 \text{ cm}^3 \cdot \text{min}^{-1}$.

DISCUSSION AND CONCLUSION

A new and original method of production of cyclopentanone has been prepared that reaches high values of selectivity of reacted adipic acid, or its esters. A number of catalysts and carriers have been studied. The experiments have shown that the selectivity of cyclopentanone in all the cases is relatively high, especially for the fact that it is a thermally destructive process. On the other hand, the values of conversion of the raw material considerably differed. During the reaction the catalyst covers with a layer of carbon, that leads to decreased activity. This decrease after start-up is more rapid. Only in a short time (cca 0.5 hour) it relatively slows down. After about two days it again considerably decreases. However, the catalyst can be easily regenerated by burning in oxygen or air at temperatures between 500°C and 600°C. The catalytic activity of the catalyst becomes renewed. This decrease of service life of the catalyst has been typical not only for the described catalyst (see Table 2.) but also for other types of monitored catalysts.

On the basis of these laboratory measurements an experimental production of cyclopentanone was designed and started in the company Chemko Strážske, a.s. So far 25 tonnes of cyclopentanone of high quality have been produced.

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